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Symmetries and independent components of Coulomb integrals

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The Coulomb integrals, i.e. the matrix elements of the Coulomb potential between one-electron orbitals, are basic objects of electronic structure calculations. In this paper Coulomb integrals are analyzed in terms of the symmetry of the crystal or molecule. We consider the case where the one-electron orbitals form the basis of a real, complex or pseudo-complex irreducible representation. We take into account both the symmetry group of the site and the permutation symmetries of Coulomb integrals. We provide explicit formulas to calculate all Coulomb integrals in terms of the minimum number of independent invariant integrals, that we enumerate. We give explicit formulas relating the Coulomb integrals of a symmetry group to the ones of a subgroup, taking the example of spherically symmetric orbitals. The group-theory techniques that we use include Clebsch-Gordan coefficients, co-representations of magnetic groups, recoupling formulas and the Racah factorization theorem.

PACS numbers:

I. INTRODUCTION

The problem of the number of independent components of Coulomb matrix elements is important from several points of view. In the analysis of spectroscopic data, this number is the number of parameters to fit, in electronic structure calculation it is the minimal number of time-consuming double integrals to calculate. This problem was famously investigated by Tanabe, Sugano and Kamimura¹ for d -shell electrons in octahedral O_h symmetry and more recently extended by Bünemann and Gebhard for d - and f -shell in O_h , O , T_d , T_h , D_{6h} and D_{4h} symmetries².

We extend their work in several directions. We deal with any orbital and any group, we consider all types of irreducible representations whereas previous works dealt only with real representations (i.e. wavefunctions) and we give explicit expressions for the independent components and for the relation between arbitrary Coulomb integrals and the independent ones. Moreover, we describe Coulomb integrals of a subgroup in terms of those of a larger group.

This is the first of a series of papers investigating the behavior of Coulomb matrix elements as a function of symmetry, covalence and electronic relaxation. This more theoretical paper will be followed by the discussion of cubic materials (e.g. NiO) and then to materials with lower symmetries.

We now give the outline of this paper. It starts with a discussion of the various symmetries of Coulomb integrals for complex and real one-electron orbitals. In particular, we consider the case when the one-electron orbitals are bases of irreducible representations of a group G . Then, we use the Clebsch-Gordan coefficients of G to define linear combinations of Coulomb integrals (called G -invariants) that are invariant under the action of the operations of G and we show that all Coulomb integrals can be written in terms of these G -invariants. The next section describes the way to take permutation symmetries into account. This further reduces the number of independent integrals, which are now (permutation)-symmetrized G -invariants. We give an explicit formula for the calculation of any Coulomb integral in terms of these symmetrized G -invariants and we show, conversely, that symmetrized G -invariants can be calculated from the same number of well-chosen Coulomb integrals. For the example of d orbitals in cubic symmetries, 625 Coulomb integrals can be obtained from the computation of only ten of them. Finally we deal with the problem of symmetry breaking by considering G as a subgroup of the infinite group $O(3)$ of rotations and inversion of three-dimensional space. We express G -invariants in terms of $O(3)$ -invariants (i.e. Slater integrals), which can be used to quantify the deviation of the system from spherical symmetry. We close the paper with some concluding remarks and possible extensions of our work.

II. INVARIANCE OF COULOMB INTEGRALS

In this section, we first show that Coulomb integrals are invariant under the action of isometries and we discuss what happens when the one-electron orbitals are bases of irreducible representations. Then, we study the invariance of Coulomb integrals under permutations of one-electron orbitals.

A. Change of variable

Let us define a Coulomb integral by

$$U_{abcd} = \langle \varphi_a \varphi_b | V | \varphi_c \varphi_d \rangle = \int d\mathbf{x} d\mathbf{y} \frac{\varphi_a^*(\mathbf{x}) \varphi_b^*(\mathbf{y}) \varphi_c(\mathbf{x}) \varphi_d(\mathbf{y})}{|\mathbf{x} - \mathbf{y}|}, \quad (1)$$

where $\varphi_a, \varphi_b, \varphi_c$ and φ_d are one-electron orbitals. We carry out the change of variable $\mathbf{x} = \rho \mathbf{x}'$, $\mathbf{y} = \rho \mathbf{y}'$, where ρ is an isometry. We recall that any isometry can be written $\rho \mathbf{x} = R \mathbf{x} + \mathbf{t}$, where R is a rotation or a rotation multiplied by an inversion, and \mathbf{t} is a translation. Since an isometry conserves volumes we have $d\mathbf{x} = d\mathbf{x}'$, $d\mathbf{y} = d\mathbf{y}'$. Moreover $|\mathbf{x} - \mathbf{y}| = |\mathbf{x}' - \mathbf{y}'|$ because the distance between two points is invariant under isometry. We obtain

$$U_{abcd} = \int d\mathbf{x}' d\mathbf{y}' \frac{\varphi_a^*(\rho \mathbf{x}') \varphi_b^*(\rho \mathbf{y}') \varphi_c(\rho \mathbf{x}') \varphi_d(\rho \mathbf{y}')}{|\mathbf{x}' - \mathbf{y}'|}. \quad (2)$$

B. Invariance under point symmetry operations

We assume now that the system is invariant under the operations R of a point symmetry group G . This means that, if φ_a is an orbital of the system, then the transformation of φ_a by a symmetry operation R of G is again an orbital of the system with the same energy.

In a more abstract way, the action of a group G on a set X is an operation that associates to each pair (g, x) with g in G and x in X , an element of X denoted by $g \triangleright x$. Moreover, this operation satisfies $1 \triangleright x = x$ and $g \triangleright (g' \triangleright x) = (g \cdot g') \triangleright x$.

For example if $X = \mathbb{R}^3$ and G is a point symmetry group defined by matrices R , then $R \triangleright \mathbf{x} = R \mathbf{x}$. In molecular or solid-state physics we deal with a set X of orbitals φ_a . Then $(R \triangleright \varphi_a)(\mathbf{x}) = \varphi_a(R^{-1} \mathbf{x})$ (the variable \mathbf{x} is replaced by $R^{-1} \mathbf{x}$ in φ_a). Indeed

$$(R \triangleright (S \triangleright \varphi_a))(\mathbf{x}) = (R \triangleright \varphi_a)(S^{-1} \mathbf{x}) = \varphi_a(S^{-1} R^{-1} \mathbf{x}) = \varphi_a((RS)^{-1} \mathbf{x}) = ((RS) \triangleright \varphi_a)(\mathbf{x}).$$

In that sense, Eq. (2) can be written

$$\rho^{-1} \triangleright U_{abcd} = U_{abcd}. \quad (3)$$

In fact, Eq. (2) says that Coulomb integrals $\langle \varphi_a \varphi_b | V | \varphi_c \varphi_d \rangle$ are invariant under the action of any isometry, but we restrict it here to the case of elements of G . This is because we can then describe the action of R on φ_a by a matrix representation. In other words, we consider that there exist matrices $\Gamma(R)$ such that $\Gamma(R)\Gamma(S) = \Gamma(RS)$ for any R and S in G and

$$R \triangleright \varphi_a = \sum_b \Gamma_{ba}(R) \varphi_b, \quad (4)$$

where the order of the indices of Γ is required³ (p. 65) to get

$$\begin{aligned} R \triangleright (S \triangleright \varphi_a) &= \sum_b \Gamma_{ba}(S) (R \triangleright \varphi_b) = \sum_{bc} \Gamma_{ba}(S) \Gamma_{cb}(R) \varphi_c = \sum_c (\Gamma(R) \Gamma(S))_{ca} \varphi_c = \sum_c (\Gamma(RS))_{ca} \varphi_c \\ &= (RS) \triangleright \varphi_a. \end{aligned}$$

We are particularly interested in irreducible representations. There are three types of irreducible representations (in the sense of Frobenius-Schur⁴): (a) real irreps, for which we can find real representation matrices $\Gamma(R)$; (b) complex, for which $\Gamma(R)^*$ does not represent the same irrep as $\Gamma(R)$ (e.g. $e^{i\mathbf{k}\cdot\mathbf{r}}$ for the translation group); and (c) pseudo-real (quaternionic) for which $\Gamma(R)^*$ represents the same irrep as $\Gamma(R)$ but the representation matrices cannot all be real. If the wavefunctions are real, then the matrix representation is real. Indeed

$$(R \triangleright \varphi_a)(\mathbf{x}) = \varphi_a(R^{-1} \mathbf{x}) = \sum_b \Gamma_{ba}(R) \varphi_b(\mathbf{x}).$$

Therefore

$$\Gamma_{ba}(R) = \int d\mathbf{x} \varphi_b^*(\mathbf{x}) \varphi_a(R^{-1} \mathbf{x}) = \int d\mathbf{x} \varphi_b^*(R \mathbf{x}) \varphi_a(\mathbf{x}), \quad (5)$$

is real if φ_a and φ_b are real. However, even when the representation is real in the sense of Frobenius-Schur, its matrix representation can contain non-real complex numbers. For example, E_g is a real irreducible representation of O_h , but its matrix representation contains non-real numbers in Altmann and Herzig's tables⁵. For the groups O_h , O , T_d , D_{6h} and D_{4h} investigated by Bünemann and Gebhard², all irreducible representations are real. For the last group T_h studied in that article, there are four complex one-dimensional representations (${}^1E_g, {}^2E_g, {}^1E_u, {}^2E_u$). They can be grouped into pairs to become real two-dimensional (but no longer irreducible).

Let α, β, γ and δ be irreducible representations of G . For each of these representations, for instance α , let $\phi_a^{(\alpha)}$ with $a = 1, \dots, \dim \alpha$ be a basis of this representation. Define

$$U_{abcd}^{(\alpha\beta\gamma\delta)} = \langle \varphi_a^{(\alpha)} \varphi_b^{(\beta)} | V | \varphi_c^{(\gamma)} \varphi_d^{(\delta)} \rangle.$$

Then, Eq. (4) yields

$$R \triangleright U_{abcd}^{(\alpha\beta\gamma\delta)} = \sum_{a'b'c'd'} \Gamma_{a'a}^{(\alpha)}(R) \Gamma_{b'b}^{(\beta)}(R) \Gamma_{c'c}^{(\gamma)}(R) \Gamma_{d'd}^{(\delta)}(R) U_{a'b'c'd'}^{(\alpha\beta\gamma\delta)}.$$

Thus, the invariance relation Eq. (2) implies

$$R \triangleright U_{abcd}^{(\alpha\beta\gamma\delta)} = \sum_{a'b'c'd'} \Gamma_{a'a}^{(\alpha)}(R) \Gamma_{b'b}^{(\beta)}(R) \Gamma_{c'c}^{(\gamma)}(R) \Gamma_{d'd}^{(\delta)}(R) U_{a'b'c'd'}^{(\alpha\beta\gamma\delta)} = U_{abcd}^{(\alpha\beta\gamma\delta)}, \quad (6)$$

for every $R \in G$.

C. Invariance under some permutations

We describe now additional symmetries of the Coulomb integrals, which are different when the orbitals are complex and real. Let us start by complex orbitals.

1. Complex orbitals

If we interchange \mathbf{x}' and \mathbf{y}' in the definition (1) of U_{abcd} we obtain $U_{abcd} = U_{badc}$, and if we take the complex conjugate we obtain $U_{abcd}^* = U_{cdab}$. As a consequence,

$$U_{abcd} = U_{badc} = U_{cdab}^* = U_{dcba}^*. \quad (7)$$

This means that the Coulomb integrals are invariant under the action of a group G_σ of 4 permutations $G_\sigma = \{\sigma_1, \sigma_2, \sigma_3, \sigma_4\}$ defined

$$\sigma_1(abcd) = (abcd), \quad \sigma_2(abcd) = (badc), \quad \sigma_3(abcd) = (cdab), \quad \sigma_4(abcd) = (dcba),$$

with actions

$$\sigma_1 \triangleright U_{abcd} = U_{abcd}, \quad \sigma_2 \triangleright U_{abcd} = U_{badc}, \quad \sigma_3 \triangleright U_{abcd} = U_{cdab}^*, \quad \sigma_4 \triangleright U_{abcd} = U_{dcba}^*.$$

Because of the presence of a complex conjugation in the action of G_σ , we do not have a representation but a corepresentation, as defined by Wigner⁶ and G_σ is a magnetic group, and more precisely the Shubnikov group of the IIIrd kind $m'm2'$.

2. Real orbitals

For real orbitals φ_i , we have also $U_{1234} = U_{3214} = U_{1432}$ and the symmetries are²

$$U_{abcd} = U_{badc} = U_{cdab} = U_{dcba} = U_{cbad} = U_{dabc} = U_{adcb} = U_{bcda}. \quad (8)$$

These symmetries form a group G_σ of order 8, which is a subgroup of the group \mathcal{S}_4 of permutation of 4 elements. It can be seen that G_σ is equivalent to the symmetry group D_4 of the square. Indeed, if we denote by a, b, c, d the four consecutive corners of a square, the group operations of D_4 give us then $C_4 \mapsto (dabc)$, $C_4^2 \mapsto (cdab)$, $C_4^3 \mapsto (bcda)$, $C_2' \mapsto (dcba)$, $C_2'' \mapsto (badc)$, $C_2''' \mapsto (adcb)$, $C_2'''' \mapsto (cbad)$.

When orbitals are real, we can use the more advanced framework of the theory of group representations (instead of corepresentations).

III. GROUP INVARIANTS

In this section we deal only with the invariance of the Coulomb integrals under the action of the point symmetry group G . For notational convenience, we make hypothesis (H): the product of two irreducible representations of G is a sum of irreducible representations of G where no representation appears twice. By definition, all simply-reducible groups^{7,8} satisfy (H) but simple reducibility additionally requires additional properties. Group $O(3)$ is simply-reducible as well as all point groups except for⁹: C_3 , C_4 , C_6 , C_{3h} , C_{4h} , C_{6h} , S_4 , S_6 , T and T_h . We see in point group tables⁵ that they all satisfy (H), except for T and T_h . In group T , the only breaking of (H) comes in the square of irrep T , which contains irrep T twice. Similarly, in group T_h , irrep T_g is contained twice in the square of irrep T_g . However, these two copies of T (resp. T_g) are uniquely defined because one belongs to the symmetric product and the other to the antisymmetric product of T (resp. T_g). In that sense, all point groups satisfy (H). In any case, the present treatment can be extended to groups which do not satisfy condition (H) by following methods which are now standard in the literature^{10–16}, but the resulting cluttering of indices becomes confusing.

In this section we define so-called G -invariants, which are objects enjoying an invariance under basis change and under the action of any element of G . Then, we show that all Coulomb matrix elements can be written in terms of these G -invariants.

A. Clebsch-Gordan coefficients

For any finite (or compact) group G , the tensor (or direct or Kronecker³) product of two irreducible representations can be written as a sum of representations. The *Clebsch-Gordan coefficients* describe the coefficients of this sum. More precisely, we define Clebsch-Gordan coefficients $(\alpha\beta b|\phi f)$ as any set of complex numbers solving the equation³ (p. 85)

$$\Gamma_{a'a}^{(\alpha)}(R)\Gamma_{b'b}^{(\beta)}(R) = \sum_{\phi ff'} (\alpha a' \beta b' | \phi f') \Gamma_{f'f}^{(\phi)}(R) (\alpha\beta b | \phi f)^*. \quad (9)$$

A possible solution of this equation is given by Dirac's formula¹⁷

$$(\alpha\beta b | \eta e) = \sqrt{\frac{\dim \eta}{|G|}} \frac{\sum_R \Gamma_{aa_0}^{(\alpha)}(R) \Gamma_{bb_0}^{(\beta)}(R) (\Gamma_{ee_0}^{(\eta)}(R))^*}{\sqrt{\sum_R \Gamma_{a_0 a_0}^{(\alpha)}(R) \Gamma_{b_0 b_0}^{(\beta)}(R) (\Gamma_{e_0 e_0}^{(\eta)}(R))^*}}. \quad (10)$$

where, $|G|$ is the number of elements of G and, for each triple (α, β, η) , three components (a_0, b_0, e_0) are chosen so that $\sum_R \Gamma_{a_0 a_0}^{(\alpha)}(R) \Gamma_{b_0 b_0}^{(\beta)}(R) \Gamma_{e_0 e_0}^{(\eta)}(R) \neq 0$. Such components exist if η is in the tensor product of α and β (see also¹⁸ (p. 105)).

This definition of Clebsch-Gordan coefficients as any solution of Eq. (9) is inspired by Derome and Sharp³⁷. Note that this definition does not fully specify Clebsch-Gordan coefficients, since multiplying them by a phase depending on α , β and γ transforms a solution into another one. Other approaches use careful choices of these phases to maximize the symmetry of Clebsch-Gordan coefficients^{12,14–16,19–21}. However, these phases depend on each group and the Clebsch-Gordan coefficients given by Dirac's formula (10) generally do not satisfy these symmetries. Another advantage of the work by Derome and Sharp is that they give the recoupling formula that we need in this paper, whereas it is not present in¹⁴ or²⁰. A third advantage is more technical but turns out to be crucial³⁸.

These Clebsch-Gordan coefficients are a generalization of the ones used in angular momentum theory. They satisfy similar orthogonality relations³ (p. 84):

$$\sum_{ab} (\alpha\beta b | \eta e)^* (\alpha\beta b | \phi f) = \delta_{\eta\phi} \delta_{ef}, \quad (11)$$

$$\sum_{\eta e} (\alpha\beta b | \eta e)^* (\alpha' \beta b' | \eta e) = \delta_{\alpha\alpha'} \delta_{bb'}. \quad (12)$$

This means that the Clebsch-Gordan coefficients of the groups considered in this paper can be considered as matrix elements of a unitary matrix.

B. Coulomb G -invariants

As a first step of the symmetry analysis of Coulomb matrix elements $U_{abcd}^{(\alpha\beta\gamma\delta)}$ for given irreps α , β , γ and δ , we define the corresponding G -invariants as

$$I^{(\alpha\beta\gamma\delta,\eta)} = \frac{1}{\dim \eta} \sum_{abcde} U_{abcd}^{(\alpha\beta\gamma\delta)} (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e), \quad (13)$$

where η belongs to the irrep expansion of both $\alpha \otimes \beta$ and $\gamma \otimes \delta$. Note that, because of the basis transformation rules for $U_{abcd}^{(\alpha\beta\gamma\delta)}$ and Clebsch-Gordan coefficients, $I^{(\alpha\beta\gamma\delta,\eta)}$ is basis-independent. This means that G -invariants can be compared even if the representation matrices of irreps are different. However, if $(\gamma, \delta) \neq (\alpha, \beta)$ they can differ from one another by a phase due to the phase ambiguity of Clebsch-Gordan coefficients.

We can interpret Eq. (13) in terms of matrix elements. Indeed

$$U_{abcd}^{(\alpha\beta\gamma\delta)} = \langle \varphi_a^{(\alpha)} \varphi_b^{(\beta)} | V | \varphi_c^{(\gamma)} \varphi_d^{(\delta)} \rangle.$$

Therefore,

$$I^{(\alpha\beta\gamma\delta,\eta)} = \frac{1}{\dim \eta} \sum_e \langle (\varphi^{(\alpha)} \otimes \varphi^{(\beta)})_e^{(\eta)} | V | (\varphi^{(\gamma)} \otimes \varphi^{(\delta)})_e^{(\eta)} \rangle,$$

where Clebsch-Gordan coefficients are used to couple irreps:

$$(\varphi^{(\alpha)} \otimes \varphi^{(\beta)})_e^{(\eta)} = \sum_{ab} (\alpha a \beta b | \eta e) \varphi_a^{(\alpha)} \otimes \varphi_b^{(\beta)}, \quad (\varphi^{(\gamma)} \otimes \varphi^{(\delta)})_e^{(\eta)} = \sum_{cd} (\gamma c \delta d | \eta e) \varphi_c^{(\gamma)} \otimes \varphi_d^{(\delta)}.$$

We now state two important results. The first is the fact that, for any value of the complex numbers $U_{abcd}^{(\alpha\beta\gamma\delta)}$ (where $a = 1, \dots, \dim \alpha$, $b = 1, \dots, \dim \beta$, $c = 1, \dots, \dim \gamma$, $d = 1, \dots, \dim \delta$), which transform under the operation of G as the product of irreps $\alpha \otimes \beta \otimes \gamma \otimes \delta$,

$$R \triangleright I^{(\alpha\beta\gamma\delta,\eta)} = \frac{1}{\dim \eta} \sum_{abcd a' b' c' d' e} \Gamma_{a'a}^*(R) \Gamma_{b'b}^*(R) \Gamma_{c'c}(R) \Gamma_{d'd}(R) U_{a'b'c'd'}^{(\alpha\beta\gamma\delta)} (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) = I^{(\alpha\beta\gamma\delta,\eta)}.$$

In other words, $I^{(\alpha\beta\gamma\delta,\eta)}$ is invariant under the action of G even if the coefficients $U_{abcd}^{(\alpha\beta\gamma\delta)}$ are not (we just assumed that they transform as products of irreps).

The second result is a consequence of Schur's lemma: if $U_{abcd}^{(\alpha\beta\gamma\delta)}$ is invariant under the action of G (i.e. satisfies Eq. (6)), then the matrix $U_{abcd}^{(\alpha\beta\gamma\delta)}$ is diagonalized by the Clebsch-Gordan coefficients and its eigenvalues are $I^{(\alpha\beta\gamma\delta,\eta)}$:

$$\sum_{abcd} (\alpha a \beta b | \phi f)^* U_{abcd}^{(\alpha\beta\gamma\delta)} (\gamma c \delta d | \eta e) = \delta_{\phi\eta} \delta_{ef} I^{(\alpha\beta\gamma\delta,\eta)}. \quad (14)$$

As a consequence, any $U_{abcd}^{(\alpha\beta\gamma\delta)}$ can be written explicitly in terms of G -invariants:

$$U_{abcd}^{(\alpha\beta\gamma\delta)} = \sum_{\eta e} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e)^* I^{(\alpha\beta\gamma\delta,\eta)}. \quad (15)$$

This shows that, if η runs over the irreps common to $\alpha \otimes \beta$ and $\gamma \otimes \delta$, then the set of $I^{(\alpha\beta\gamma\delta,\eta)}$ forms a complete family of G -invariants generating $U_{abcd}^{(\alpha\beta\gamma\delta)}$. As a consequence, their number can be obtained by the character formula

$$n^{(\alpha\beta\gamma\delta)} = \frac{1}{|G|} \sum_R \chi^\alpha(R)^* \chi^\beta(R)^* \chi^\gamma(R) \chi^\delta(R), \quad (16)$$

where, for each irrep η , $\chi^\eta(R) = \text{Tr}(\Gamma^{(\eta)}(R))$.

However, this number does not take into account the permutation symmetries described in section II C. These symmetries considerably decrease the number of invariants and are discussed in the next section.

IV. PERMUTATION INVARIANTS

In this section, we consider the effect of permutation symmetries described in Eq. (8) for real representations and in Eq. (7) for non-real representations.

A. Real representations

In this section we assume that all irreps are real and that they are represented by real matrices. Up to now, the coefficients $U_{abcd}^{(\alpha\beta\gamma\delta)}$ were not supposed to have any permutation symmetry. To impose the D_4 permutation symmetry of real Coulomb integrals, we project each coefficient on the fully symmetric irrep of D_4 . This is done by replacing each $U_{abcd}^{(\alpha\beta\gamma\delta)}$ by its symmetrization

$$\begin{aligned} \langle U_{abcd}^{(\alpha\beta\gamma\delta)} \rangle &= \frac{1}{|D_4|} \sum_{\sigma \in D_4} U_{\sigma(abcd)}^{\sigma(\alpha\beta\gamma\delta)} \\ &= \frac{1}{8} (U_{abcd}^{(\alpha\beta\gamma\delta)} + U_{badc}^{(\beta\alpha\delta\gamma)} + U_{cdab}^{(\gamma\delta\alpha\beta)} + U_{dcba}^{(\delta\gamma\beta\alpha)} + U_{cbad}^{(\gamma\beta\alpha\delta)} + U_{dabc}^{(\delta\alpha\beta\gamma)} + U_{adcb}^{(\alpha\delta\gamma\beta)} + U_{bcda}^{(\beta\gamma\delta\alpha)}). \end{aligned} \quad (17)$$

We obtain the symmetrized G -invariant

$$\begin{aligned} \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle &= \frac{1}{8 \dim \eta} \left(\sum_{abcde} U_{abcd}^{(\alpha\beta\gamma\delta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) + \sum_{abcde} U_{badc}^{(\beta\alpha\delta\gamma)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) \right. \\ &\quad + \sum_{abcde} U_{cdab}^{(\gamma\delta\alpha\beta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) + \sum_{abcde} U_{dcba}^{(\delta\gamma\beta\alpha)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) \\ &\quad + \sum_{abcde} U_{cbad}^{(\gamma\beta\alpha\delta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) + \sum_{abcde} U_{dabc}^{(\delta\alpha\beta\gamma)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) \\ &\quad \left. + \sum_{abcde} U_{adcb}^{(\alpha\delta\gamma\beta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) + \sum_{abcde} U_{bcda}^{(\beta\gamma\delta\alpha)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) \right), \end{aligned} \quad (18)$$

where we used the fact that, when irreps are real, the corresponding Clebsch-Gordan coefficients can be chosen real. The purpose of the next two sections is to write the symmetrized G -invariants $\langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle$ in terms of the unsymmetrized ones. More precisely, we project the G -invariants onto the symmetrized ones.

B. The first four terms

The purpose of this section is to write the symmetrized G -invariants $\langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle$ in terms of the unsymmetrized ones. Two terms in the right hand side of Eq. (18) are obvious:

$$\begin{aligned} \sum_{abcde} U_{abcd}^{(\alpha\beta\gamma\delta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) &= I^{(\alpha\beta\gamma\delta,\eta)} \dim \eta, \\ \sum_{abcde} U_{cdab}^{(\gamma\delta\alpha\beta)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) &= \sum_{abcde} U_{cdab}^{(\gamma\delta\alpha\beta)} (\gamma c \delta d | \eta e) (\alpha a \beta b | \eta e) = I^{(\gamma\delta\alpha\beta,\eta)} \dim \eta. \end{aligned}$$

To deal with two other terms, we notice that, as a consequence of Schur's lemma, the Clebsch-Gordan coefficients $(\alpha a \beta b | \eta e)$ and $(\beta b \alpha a | \eta e)$ differ by at most a phase depending on α , β and η (but not on a , b and e). We denote this phase by $\{\alpha\beta, \eta\}$ ²⁰ (p. 231),¹⁴ (p. 57) and, for real Clebsch-Gordan coefficients $\{\alpha\beta, \eta\} = \pm 1$. In other words,

$$(\alpha a \beta b | \eta e) = \{\alpha\beta, \eta\} (\beta b \alpha a | \eta e).$$

This enables us to write

$$\begin{aligned} \sum_{abcde} U_{badc}^{(\beta\alpha\delta\gamma)} (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e) &= \{\alpha\beta, \eta\} \{\gamma\delta, \eta\} \sum_{abcde} U_{badc}^{(\beta\alpha\delta\gamma)} (\beta b \alpha a | \eta e) (\delta d \gamma c | \eta e) = \{\alpha\beta, \eta\} \{\gamma\delta, \eta\} I^{(\beta\alpha\delta\gamma,\eta)} \dim \eta, \\ \sum_{abcde} U_{dcba}^{(\delta\gamma\beta\alpha)} (\beta b \alpha a | \eta e) (\delta d \gamma c | \eta e) &= \{\alpha\beta, \eta\} \{\gamma\delta, \eta\} \sum_{abcde} U_{dcba}^{(\delta\gamma\beta\alpha)} (\delta d \gamma c | \eta e) (\beta b \alpha a | \eta e) = \{\alpha\beta, \eta\} \{\gamma\delta, \eta\} I^{(\delta\gamma\beta\alpha,\eta)} \dim \eta. \end{aligned}$$

C. The last four terms

The last four terms are more tricky. Indeed, the Clebsch-Gordan coefficients do not couple the first and the second irreps, and then the third and fourth irreps, they couple for instance the first and the fourth irreps, as well as the second and the third. As a consequence, we need to use the recoupling formula proposed by Derome and Sharp, which is valid for general Clebsch-Gordan coefficients.

1. Recoupling of irreps

Derome and Sharp give a recoupling formula for general Clebsch-Gordan coefficients (Theorem 3 of ¹⁰ which, for real representation matrices (and multiplicity-free point groups), takes the form

$$\sum_e (\alpha\alpha\beta b|\eta e)(\gamma c\delta d|\eta e) = \dim \eta \sum_{\phi f} (-1)^{\phi+\eta} \begin{Bmatrix} \alpha & \beta & \eta \\ \gamma & \delta & \phi \end{Bmatrix} (\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f), \quad (19)$$

where the $6j$ -symbols are defined by³⁹

$$\begin{Bmatrix} \alpha & \beta & \eta \\ \gamma & \delta & \phi \end{Bmatrix} = \frac{(-1)^{\alpha+\beta+\eta+\gamma+\delta+\phi}}{\dim \eta \dim \phi} \sum_{abcdef} (\gamma c\delta d|\eta e)(\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f)(\alpha a\beta b|\eta e). \quad (20)$$

In Eqs. (19) and (20), the symbols $(-1)^\alpha$, $(-1)^\beta$, etc... are defined as follows. Following Derome and Sharp we first define $1j$ -symbols by $(\alpha)_{aa'} = (\alpha a 0 0|\alpha a')$, where 0 is the fully-symmetric irrep. By Schur's lemma, it can be shown that $(\alpha)_{aa'} = \pm \delta_{aa'}$ and we denote the sign \pm by $(-1)^\alpha$. In particular, if Clebsch-Gordan coefficients are calculated from Dirac's formula Eq. (10), then $(-1)^\alpha = 1$ for every irrep α . We also use the obvious notation $(-1)^{\phi+\eta} = (-1)^\phi (-1)^\eta$.

In the literature, other $6j$ symbols were defined which enjoy nice symmetry properties^{14,20}. However, these symmetries require to adjust the phases of the Clebsch-Gordan coefficients. We follow again Derome's approach and work with general Clebsch-Gordan coefficients^{10,11,22}.

2. Recoupling the last four terms

We are now ready to apply the remaining permutations of D_4 to $I^{(\alpha\beta\gamma\delta,\eta)}$. For example

$$\begin{aligned} (13) \triangleright I^{(\alpha\beta\gamma\delta,\eta)} &= \frac{1}{\dim \eta} \sum_{abcde} U_{cbad}^{(\gamma\beta\alpha\delta)} (\alpha\alpha\beta b|\eta e)(\gamma c\delta d|\eta e) \\ &= \sum_{\phi} (-1)^{\phi+\eta} \begin{Bmatrix} \alpha & \beta & \eta \\ \gamma & \delta & \phi \end{Bmatrix} \sum_{abcdf} U_{cbad}^{(\gamma\beta\alpha\delta)} (\gamma c\beta b|\phi f)(\alpha a\delta d|\phi f) = \sum_{\phi} (-1)^{\phi+\eta} \dim \phi \begin{Bmatrix} \alpha & \beta & \eta \\ \gamma & \delta & \phi \end{Bmatrix} I^{(\gamma\beta\alpha\delta,\phi)}. \end{aligned}$$

By treating the last three times in the same way, we obtain the D_4 symmetrization of $I^{(\alpha\beta\gamma\delta,\eta)}$ to be

$$\begin{aligned} \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle &= \frac{1}{8} \left(I^{(\alpha\beta\gamma\delta,\eta)} + I^{(\gamma\delta\alpha\beta,\eta)} + \{\alpha\beta, \eta\} \{\gamma\delta, \eta\} (I^{(\beta\alpha\delta\gamma,\eta)} + I^{(\delta\gamma\beta\alpha,\eta)}) \right) \\ &+ \frac{1}{8} \sum_{\phi} (-1)^{\eta+\phi} \dim \phi \begin{Bmatrix} \alpha & \delta & \phi \\ \gamma & \beta & \eta \end{Bmatrix} \left(I^{(\alpha\delta\gamma\beta,\phi)} + I^{(\gamma\beta\alpha\delta,\phi)} + \{\alpha\delta, \phi\} \{\beta\gamma, \phi\} (I^{(\delta\alpha\beta\gamma,\phi)} + I^{(\beta\gamma\delta\alpha,\phi)}) \right). \quad (21) \end{aligned}$$

3. Enumeration of symmetrized G -invariants

As noticed in ², the number of symmetrized G -invariants can be obtained from the character of the action of $G \times D_4$ on $U^{(\beta\beta\beta\alpha,\phi)}$ with elements (R, p) , which is

$$\chi^S(R, p) = \sum_{(\alpha\beta\gamma\delta) \in S} \delta_{(\alpha\beta\gamma\delta), p(\alpha\beta\gamma\delta)} \sum_{abcd} \Gamma_{a'a}^{(\alpha)}(R) \Gamma_{b'b}^{(\beta)}(R) \Gamma_{c'c}^{(\gamma)}(R) \Gamma_{d'd}^{(\delta)}(R) \Big|_{(a'b'c'd')=p^{-1}(abcd)}.$$

where S is a set of quadruples $(\alpha, \beta, \gamma, \delta)$ of irreps linked by D_4 , and $(\alpha\beta\gamma\delta)$ an element in this set. The number of symmetrized G -invariants (i.e. invariant under $G \times D_4$) is

$$n^S = \frac{1}{8|G|} \sum_{R,p} \chi^S(R, p). \quad (22)$$

We give a formula for $\chi^S(R, p)$ in terms of the characters of G for every possible set S .

- $S_1 = \{(\alpha, \alpha, \alpha, \alpha)\}$. Then

$$\sum_p \chi^{S_1}(R, p) = \chi^\alpha(R)^4 + 3\chi^\alpha(R^2)^2 + 2\chi^\alpha(R^2)\chi^\alpha(R)^2 + 2\chi^\alpha(R^4). \quad (23)$$

- $S_2 = \{(\alpha, \beta, \alpha, \beta), (\beta, \alpha, \beta, \alpha)\}$ with $\beta \neq \alpha$.

$$\sum_p \chi^{S_2}(R, p) = 2(\chi^\alpha(R)^2 + \chi^\alpha(R^2))(\chi^\beta(R)^2 + \chi^\beta(R^2)). \quad (24)$$

- $S_3 = \{(\alpha, \alpha, \beta, \beta), (\alpha, \beta, \beta, \alpha), (\beta, \beta, \alpha, \alpha), (\beta, \alpha, \alpha, \beta)\}$ with $\beta \neq \alpha$.

$$\sum_p \chi^{S_3}(R, p) = 4\chi^\alpha(R)^2\chi^\beta(R)^2 + 4\chi^\alpha(R^2)\chi^\beta(R^2). \quad (25)$$

- $S_4 = \{(\alpha, \beta, \alpha, \gamma), (\alpha, \gamma, \alpha, \beta), (\beta, \alpha, \gamma, \alpha), (\gamma, \alpha, \beta, \alpha)\}$ where $\beta \neq \alpha$ and $\beta \neq \gamma$ (but $\gamma = \alpha$ is allowed).

$$\sum_p \chi^{S_4}(R, p) = 4(\chi^\alpha(R)^2 + \chi^\alpha(R^2))\chi^\beta(R)\chi^\gamma(R). \quad (26)$$

- All the other cases

$$\sum_p \chi^{S_5}(R, p) = 8\chi^\alpha(R)\chi^\beta(R)\chi^\gamma(R)\chi^\delta(R). \quad (27)$$

4. Projection

Notice that the symmetrization described by Eq. (17) is a projection onto the fully symmetric irrep of D_4 . The matrix M transforming unsymmetrized G -invariants into symmetrized ones, which is defined by Eq. (21), is summarized by the equation

$$\langle I^{(Q, \eta)} \rangle = \sum_{Q' \in S, \phi} M_{Q\eta, Q'\phi} I^{(Q', \phi)}, \quad (28)$$

where S is one of the sets described in section IV C 3, Q and Q' run over the sets $(\alpha_1\alpha_2\alpha_3\alpha_4)$ of S . Since the symmetrization is defined as a projection, the matrix M is a projection matrix (i.e. $M^2 = M$), which is generally not orthogonal (i.e. $M^T \neq M$). The symmetrized G -invariants can also be called $G \times D_4$ -invariants because they are invariant under both G and D_4 .

5. Minimizing Coulomb integral calculations

The previous sections enabled us to show that all Coulomb integrals can be expressed in terms of a small number of symmetrized G -invariants. This is very handy because a large number of Coulomb integrals can be summarized by a small number of these invariants. However, this does not seem to be very useful from the computational point of view because the symmetrized G -invariants themselves are defined in terms of Coulomb integrals. In this section we show that it is enough to calculate as many (well chosen) Coulomb integrals $U_{abcd}^{\alpha\beta\gamma\delta}$ as symmetrized G -invariants to determine all Coulomb integrals.

To be more precise, we first showed that all Coulomb integrals $U_{abcd}^{\alpha\beta\gamma\delta}$ can be expressed in terms of a smaller number of G -invariants. This is Eq. (15) that we rewrite

$$U_{abcd}^{\alpha\beta\gamma\delta} = \sum_{\eta} A_{abcd, \eta}^{\alpha\beta\gamma\delta} I^{(\alpha\beta\gamma\delta, \eta)}, \quad (29)$$

where $A_{abcd, \eta}^{\alpha\beta\gamma\delta}$ is an $n \times m$ matrix, with $n = \dim \alpha \dim \beta \dim \gamma \dim \delta$ and $m = n^{(\alpha\beta\gamma\delta)}$ is given by Eq. (16).

Moreover, for real matrix representations, D_4 -permutation symmetry enables us to replace G -invariants $I^{(\alpha\beta\gamma\delta, \eta)}$ by symmetrized G -invariants $\langle I^{(\alpha\beta\gamma\delta, \eta)} \rangle$. However, symmetrization mixes different quadruples $(\alpha\beta\gamma\delta)$ belonging to

the same set S defined in section IV D 2. Therefore, we group all $A_{abcd,\eta}^{\alpha\beta\gamma\delta}$ for $Q = (\alpha\beta\gamma\delta)$ in the same S into a larger matrix $A_{abcd,\eta}^Q$ such that

$$U_{abcd}^Q = \sum_{\eta} A_{abcd,\eta}^Q I^{(Q,\eta)}, \quad (30)$$

where U_{abcd}^Q spans all $U_{abcd}^{(\alpha\beta\gamma\delta)}$ for $(\alpha\beta\gamma\delta)$ in S and the same holds for $I^{(Q,\eta)}$. The dimension of $A_{abcd,\eta}^Q$ is $|S|n \times m$, where $|S|$ is the number of elements of S .

We are now ready to use the D_4 -permutation symmetry of real integrals and replace in Eq. (30) $I^{(Q,\eta)}$ by $\langle I^{(Q,\eta)} \rangle$, where

$$\langle I^{(Q,\eta)} \rangle = \sum_{\phi} M_{\eta\phi}^{QQ'} I^{(Q',\phi)}.$$

We showed that M is a projection matrix (i.e. $M^2 = M$). However, since we want to conserve the distance between Coulomb integrals (as explained shortly in Eq (32)), we need to use another matrix $N_{\eta\phi}^{QQ'} = \sqrt{\dim \eta} M_{\eta\phi}^{QQ'} (1/\sqrt{\dim \phi})$, which is also a projection matrix. Any projection matrix is diagonalizable, and we denote the eigenvalues of N by $\lambda_q = 0$ or 1 and its eigenvectors by v^q , where $q = (Q, \phi)$. Since $N^T \neq N$, it is generally not possible to orthonormalize all its eigenvectors. However, we can define a set of orthonormal eigenvectors v^q for eigenvalue $\lambda_q = 1$ and a set of orthonormal eigenvectors v^q for eigenvalue $\lambda_q = 0$ (but eigenvectors of the first set are generally not orthogonal to eigenvectors of the second set). We assume that we have chosen such sets of eigenvectors.

Let B be the matrix with matrix elements $B_{pq} = v_p^q$, the p th component of v^q . We have $N_{pr} = \sum_q B_{pq} \lambda_q (B^{-1})_{qr}$. If we define $u^{Q,\phi} = \sum_{Q',\rho} (B^{-1})_{Q\phi,Q'\rho} \sqrt{\dim \rho} I^{(Q',\rho)}$, we obtain

$$\langle I^{(Q,\eta)} \rangle = (1/\sqrt{\dim \eta}) \sum_{Q',\rho} N_{\eta\rho}^{QQ'} \sqrt{\dim \rho} I^{(Q',\rho)} = (1/\sqrt{\dim \eta}) \sum_{Q',\phi, \lambda_{Q',\phi}=1} B_{Q\eta,Q'\phi} u^{Q',\phi}. \quad (31)$$

Indeed, the eigenvalues of a projection matrix are 1 and 0. If $\lambda_{Q',\phi} = 0$ the corresponding $u^{Q',\phi}$ does not contribute and we sum only over Q', ϕ such that $\lambda_{Q',\phi} = 1$. Therefore, B can now be considered as an $|S|m \times n^S$ matrix, where n^S , which is the number of eigenvectors of N corresponding to the eigenvalue 1, is given by Eq. (22).

Note that using the eigenvectors of N instead of the eigenvectors of M enables us to conserve the distance between Coulomb integrals. More precisely, if S is a set of quadruples $Q = \alpha_1\alpha_2\alpha_3\alpha_4$ of irreps as in section IV C 3 and if $I_{a_1a_2a_3a_4}^{(Q)}$ and $\underline{I}_{a_1a_2a_3a_4}^{(Q)}$ are two sets of Coulomb integrals, then the following distances are equal

$$\sum_{Q \in S} \sum_{a_1a_2a_3a_4} |I_{a_1a_2a_3a_4}^{(Q)} - \underline{I}_{a_1a_2a_3a_4}^{(Q)}|^2 = \sum_{Q \in S, \eta} \dim \eta |J^{(Q,\eta)} - \underline{J}^{(Q,\eta)}|^2 = \sum_{Q \in S, \phi} |u^{Q,\phi} - \underline{u}^{Q,\phi}|^2. \quad (32)$$

This identity will be useful to determine the global variation of Coulomb integrals as a function of pressure or when an atomic species is replaced by another one in the structure: the global variation of the Coulomb integrals is equal to the variation of the symmetrized G -invariants.

By using Eqs. (30) and (31), we can now write the Coulomb integrals as

$$U_{abcd}^Q = \sum_{\eta Q'\phi} A_{abcd,\eta}^Q B_{Q\eta,Q'\phi} u^{Q',\phi}, \quad (33)$$

where matrix AB has dimension $|S|n \times n^S$. Let r be the rank of AB . In general $r \leq n^S$ but let us consider the most common case where $r = n^S$. By a classical theorem of linear algebra, there is a set of r indices $a_1b_1c_1d_1, \dots, a_rb_rc_rd_r$ such that the $r \times r$ matrix P with matrix elements

$$P_{sq} = \sum_p A_{a_s b_s c_s d_s, p}^S B_{pq}, \quad (34)$$

has a non-zero determinant (i.e. it is a non-zero minor of AB). As a consequence, P is invertible and we can compute u_1, \dots, u_r from $U_{a_1b_1c_1d_1}^{Q_1}, \dots, U_{a_rb_rc_rd_r}^{Q_r}$ by $u^q = \sum_s (P^{-1})_{qs} U_{i_s j_s k_s l_s}^{Q_s}$. In other words, the n^S quantities u^q can be calculated from n^S Coulomb integrals. And since all Coulomb integrals can be computed from u^q by Eq. (33), we can calculate $|S|n$ Coulomb integrals from the computation of only n^S of them. Moreover, since AB depends only on Clebsch-Gordan coefficients, the choice of the r indices $a_1b_1c_1d_1, \dots, a_rb_rc_rd_r$ can be done once and for all for any choice of group and irreps.

D. Non-real representations

The permutation group acting by U_{abcd} , U_{badc} , U_{cdab}^* and U_{dcba}^* is isomorphic to the symmetry group of a rectangle (with vertices denoted anticlockwise by a , b , c , d). It is magnetic point group $m'm2'$ with unitary operations E and σ_y and anti-unitary operations C_{2z} and σ_x (among the 58 type III Shubnikov crystallographic point groups)²³. This is the symmetry group of a rectangle the upper half of it is black and the lower half white, where complex conjugation is represented by reversing black and white.

1. Symmetrization

Although the theory of projection onto irreducible corepresentations is not fully developed, it is clear that

$$\langle U_{abcd}^{(\alpha\beta\gamma\delta)} \rangle = \frac{1}{4} \left(U_{abcd}^{(\alpha\beta\gamma\delta)} + U_{badc}^{(\beta\alpha\delta\gamma)} + (U_{cdab}^{(\gamma\delta\alpha\beta)})^* + (U_{dcba}^{(\delta\gamma\beta\alpha)})^* \right),$$

is invariant under the operations of $m'm2'$. Therefore, the symmetrized components for non-real representations are

$$\begin{aligned} \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle &= \frac{1}{4} \left(\sum_{abcde} U_{abcd}^{(\alpha\beta\gamma\delta)} (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) + \sum_{abcde} U_{badc}^{(\beta\alpha\delta\gamma)} (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) \right. \\ &\quad \left. + \sum_{abcde} (U_{cdab}^{(\gamma\delta\alpha\beta)})^* (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) + \sum_{abcde} (U_{dcba}^{(\delta\gamma\beta\alpha)})^* (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) \right), \\ &= I^{(\alpha\beta\gamma\delta,\eta)} + \{\alpha\beta\eta\} \{\gamma\delta\eta\} I^{(\beta\alpha\delta\gamma,\eta)} + (I^{(\gamma\delta\alpha\beta,\eta)})^* + \{\alpha\beta\eta\} \{\gamma\delta\eta\} (I^{(\delta\gamma\beta\alpha,\eta)})^*. \end{aligned}$$

By similarly calculating $\langle I^{(\beta\alpha\delta\gamma,\eta)} \rangle$, $\langle I^{(\gamma\delta\alpha\beta,\eta)} \rangle$, and $\langle I^{(\delta\gamma\beta\alpha,\eta)} \rangle$, we obtain the following relations between symmetrized components:

$$\begin{aligned} \langle I^{(\beta\alpha\delta\gamma,\eta)} \rangle &= \{\alpha\beta\eta\} \{\gamma\delta\eta\} \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle, \\ \langle I^{(\gamma\delta\alpha\beta,\eta)} \rangle &= \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle^*, \\ \langle I^{(\delta\gamma\beta\alpha,\eta)} \rangle &= \{\alpha\beta\eta\} \{\gamma\delta\eta\} \langle I^{(\alpha\beta\gamma\delta,\eta)} \rangle^*. \end{aligned}$$

2. Enumeration of symmetrized G -components

The character formula for counting the number of times a given irreducible corepresentations appears is given by Newmarch²⁴. In our case, we consider the fully symmetric irreducible corepresentation, which is of type (a) , corresponding to an intertwining number $I = 1$.

A particularity of the character theory of corepresentations is that it takes into account only unitary operations (in our case the unit permutation $(\alpha\beta\gamma\delta)$ and the permutation $(\beta\alpha\delta\gamma)$). The character of the representation corresponding to permutation p is

$$\chi^S(R, p) = \sum_{(\alpha\beta\gamma\delta) \in S} \delta_{(\alpha\beta\gamma\delta), p(\alpha\beta\gamma\delta)} \sum_{abcd} \Gamma_{a'a}^{(\alpha)}(R) \Gamma_{b'b}^{(\beta)}(R) \Gamma_{c'c}^{(\gamma)}(R) \Gamma_{d'd}^{(\delta)}(R) \Big|_{(a'b'c'd')=p^{-1}(abcd)},$$

and the number of symmetrized G -components is

$$n^S = \frac{1}{2|G|} \sum_p' \sum_R \chi^S(R, p),$$

where \sum' runs only over the two permutations corresponding to unitary operations. We have only two cases:

- $S = \{(\alpha, \alpha, \beta, \beta)\}$, where α and β can be equal

$$n^S = \frac{1}{2|G|} \sum_R \left((\chi^\alpha(R))^2 \chi^\beta(R)^2 + \chi^\alpha(R^2) \chi^\beta(R^2) \right). \quad (35)$$

- All the other cases

$$n^S = \frac{1}{|G|} \sum_R \chi^\alpha(R) \chi^\beta(R) \chi^\gamma(R) \chi^\delta(R). \quad (36)$$

3. Minimizing Coulomb integral calculations

Exactly as in the case of real representation matrices treated in section IV C 5, the Coulomb integrals can be calculated from a minimum number n^S of them.

V. SUBDUCTION

In this section, we consider the point group G as a subgroup of the infinite group $O(3)$. In particular, we want to express the G -invariants and the symmetrized G -invariants in terms of parameters such as Slater integrals or Racah parameters.

A. $O(3)$ -invariants for Coulomb potential

The theory presented in the previous section does not apply directly to $O(3)$ because, although irreps ℓ are real (in the sense of Frobenius-Schur), they are usually represented by Wigner matrices $D^\ell(R)$ which can be complex. The usual basis of spherical harmonics basis Y_ℓ^m is also generally not real. This, however, has only a benign effect and we only indicate the results. We follow the notation used in Cowan's book²⁵ (p. 162): The Coulomb integrals are

$$\begin{aligned} U_{m_1 m_2 m_3 m_4}^{(\ell_1 \ell_2 \ell_3 \ell_4)} &= \langle \ell_1 m_1 \ell_2 m_2 | \frac{2}{r_{ij}} | \ell_3 m_3 \ell_4 m_4 \rangle \\ &= \sum_k R^k(\ell_1 \ell_2, \ell_3 \ell_4) \delta_{m_3 - m_1, m_2 - m_4} (-1)^{m_2 + m_3} \sqrt{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)(2\ell_4 + 1)} \\ &\quad \begin{pmatrix} \ell_1 & k & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & k & \ell_4 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_1 & k & \ell_3 \\ -m_1 & m_1 - m_3 & m_3 \end{pmatrix} \begin{pmatrix} \ell_2 & k & \ell_4 \\ -m_2 & m_2 - m_4 & m_4 \end{pmatrix}, \end{aligned}$$

where²⁵ (p. 162)

$$R^k(\ell_1 \ell_2, \ell_3 \ell_4) = \int_0^\infty dr_1 \int_0^\infty dr_2 \frac{2r_1^k}{r_2^{k+1}} P_{\ell_1}(r_1) P_{\ell_2}(r_2) P_{\ell_3}(r_1) P_{\ell_4}(r_2), \quad (37)$$

are radial integrals and we assumed real radial wavefunctions. The $3j$ symbols involving $0, 0, 0$ can only be non zero if $\ell_1 + \ell_3 + k$ and $\ell_2 + \ell_4 + k$ are even. Therefore, we can change the signs of m and permute the column in each $3j$ symbol without changing its value. As a consequence, $\ell_1 + \ell_3 + \ell_2 + \ell_4$ is even and $(-1)^{\ell_1 + \ell_3 + \ell_2 + \ell_4} = 1$.

Our $O(3)$ -invariants $I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)}$ were calculated by Cowan (Eq. (10.17) p. 282 of²⁵)

$$\begin{aligned} I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)} &= \langle (\ell_1 \otimes \ell_2)_m^\ell | \frac{2}{r_{ij}} | (\ell_3 \otimes \ell_4)_m^\ell \rangle \\ &= (-1)^{\ell_1 - \ell_3 + \ell} \sqrt{(2\ell_1 + 1)(2\ell_2 + 1)(2\ell_3 + 1)(2\ell_4 + 1)} \sum_k \begin{pmatrix} \ell_1 & k & \ell_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell_2 & k & \ell_4 \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} \ell_1 & \ell_2 & \ell \\ \ell_4 & \ell_3 & k \end{matrix} \right\} R^k(\ell_1 \ell_2, \ell_3 \ell_4), \end{aligned}$$

where the first quantity on the right hand side is independent of m , so that it can be written in the familiar form

$$I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)} = \frac{1}{2\ell + 1} \sum_{m_1 m_2 m_3 m_4 m} (\ell_1 m_1 \ell_2 m_2 | \ell m) (\ell_3 m_3 \ell_4 m_4 | \ell m) U_{m_1 m_2 m_3 m_4}^{(\ell_1 \ell_2 \ell_3 \ell_4)}.$$

In the case where $\ell_1 = \ell_2 = \ell_3 = \ell_4 = 2$ we write $F^k = R^k(22, 22)$ and we obtain

$$\begin{aligned} I^{(2^4, 0)} &= F^0 + \frac{2}{7} F^2 + \frac{2}{7} F^4, & I^{(2^4, 1)} &= F^0 + \frac{1}{7} F^2 - \frac{4}{21} F^4, \\ I^{(2^4, 2)} &= F^0 - \frac{3}{49} F^2 + \frac{4}{49} F^4, & I^{(2^4, 3)} &= F^0 - \frac{8}{49} F^2 - \frac{1}{49} F^4, \\ I^{(2^4, 4)} &= F^0 + \frac{4}{49} F^2 + \frac{1}{441} F^4. \end{aligned}$$

B. $O(3)$ -invariants for spherically symmetric potential

The expressions of the previous paragraph were obtained by explicitly assuming that the interaction potential is the Coulomb potential. In the following, we only assume that the potential is spherically symmetric (so that the invariants remain $O(3)$ -invariants) and symmetric under the exchange of particles (so that the D_4 permutation symmetry is still valid.) This enables us to consider more general effective potentials.

As in the case of the general group G , we can build $O(3)$ -invariants. The D_4 permutation symmetry can only be applied if the complex spherical harmonics are transformed into real tesseral harmonics. We can also work with spherical harmonics, but some additional signs appear. The result of permutation symmetrization (for spherical harmonics) is:

$$\begin{aligned} \langle I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)} \rangle &= \frac{1}{8} \left(I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)} + I^{(\ell_2 \ell_1 \ell_4 \ell_3, \ell)} + I^{(\ell_3 \ell_4 \ell_1 \ell_2, \ell)} + I^{(\ell_4 \ell_3 \ell_2 \ell_1, \ell)} \right. \\ &\quad \left. + (-1)^{\ell_1 + \ell_3} \sum_{\ell'} (2\ell' + 1) \begin{Bmatrix} \ell_4 & \ell_1 & \ell' \\ \ell_2 & \ell_3 & \ell \end{Bmatrix} \left(I^{(\ell_3 \ell_2 \ell_1 \ell_4, \ell')} + I^{(\ell_4 \ell_1 \ell_2 \ell_3, \ell')} + I^{(\ell_1 \ell_4 \ell_3 \ell_2, \ell')} + I^{(\ell_2 \ell_3 \ell_4 \ell_1, \ell')} \right) \right). \end{aligned}$$

In particular, if $\ell_1 = \ell_2 = \ell_3 = \ell_4$, then

$$\langle I^{(\ell_1^4, \ell)} \rangle = \frac{1}{2} I^{(\ell_1^4, \ell)} + \frac{1}{2} \sum_{\ell'} (2\ell' + 1) \begin{Bmatrix} \ell_1 & \ell_1 & \ell' \\ \ell_1 & \ell_1 & \ell \end{Bmatrix} I^{(\ell_1^4, \ell')}.$$

The number of symmetrized $O(3)$ -invariants is expressed by formulas similar to the one given for G . For example, if $\ell_1 = \ell_2 = \ell_3 = \ell_4 = \ell$, and if the rotations are defined by an axis and an angle ω , then the character of the rotation is $\chi_\ell(\omega) = \sin((2\ell + 1)\omega/2) / \sin(\omega/2)$ and²⁶ (p. 103)

$$n^{S_1} = \frac{1}{8\pi} \int_0^{2\pi} \sin^2(\omega/2) d\omega (\chi_\ell(\omega)^4 + 3\chi_\ell(2\omega)^2 + 2\chi_\ell(2\omega)\chi_\ell(\omega)^2 + 2\chi_\ell(4\omega)) = \ell + 1.$$

Similarly

$$\begin{aligned} n^{S_2} &= \min(\ell_\alpha + 1, \ell_\beta + 1), \\ n^{S_3} &= \min(2\ell_\alpha + 1, 2\ell_\beta + 1), \\ n^{S_4} &= \frac{1}{2} a^{\ell_\beta \ell_\gamma}(0) - \frac{1}{2} a^{\ell_\beta \ell_\gamma}(2\ell_\alpha + 1) + \frac{1}{2} b^{\ell_\beta \ell_\gamma}(2\ell_\alpha) \\ n^{S_5} &= a^{\ell_\alpha \ell_\beta}(|\ell_\gamma - \ell_\delta|) - a^{\ell_\alpha \ell_\beta}(\ell_\gamma + \ell_\delta + 1), \end{aligned}$$

where

$$\begin{aligned} a^{\ell\ell'}(m) &= 2 \min(\ell, \ell') + 1 \text{ for } |m| \leq |\ell - \ell'|, \\ &= \ell + \ell' - |m| + 1 \text{ for } |\ell - \ell'| \leq |m| \leq \ell + \ell', \\ &= 0 \text{ for } |m| > \ell + \ell', \end{aligned}$$

and

$$\begin{aligned} b^{\ell\ell'}(m) &= 1 \text{ if } \ell + \ell' \text{ is even and } |m| \geq |\ell - \ell'|, \\ &= -1 \text{ if } \ell + \ell' \text{ is odd and } |m| > \ell + \ell', \\ &= 0 \text{ otherwise.} \end{aligned}$$

For $\ell_1 = \ell_2 = \ell_3 = \ell_4 = 2$ we obtain $n^{S_1} = 3$ independent symmetrized $O(3)$ -invariants. Indeed

$$\begin{aligned} \langle I^{(2^4, 0)} \rangle &= \frac{3}{5} I^{(2^4, 0)} - \frac{3}{10} I^{(2^4, 1)} + \frac{1}{2} I^{(2^4, 2)} - \frac{7}{10} I^{(2^4, 3)} + \frac{9}{10} I^{(2^4, 4)}, \\ \langle I_s^{(2^4, 1)} \rangle &= -\frac{1}{10} I^{(2^4, 0)} + \frac{3}{4} I^{(2^4, 1)} - \frac{1}{4} I^{(2^4, 2)} + \frac{3}{5} I^{(2^4, 4)}, \\ \langle I^{(2^4, 2)} \rangle &= \frac{1}{10} I^{(2^4, 0)} - \frac{3}{20} I^{(2^4, 1)} + \frac{11}{28} I^{(2^4, 2)} + \frac{2}{5} I^{(2^4, 3)} + \frac{9}{35} I^{(2^4, 4)}, \\ \langle I^{(2^4, 3)} \rangle &= -\frac{1}{10} I^{(2^4, 0)} + \frac{2}{7} I^{(2^4, 2)} + \frac{3}{4} I^{(2^4, 3)} + \frac{9}{140} I^{(2^4, 4)}, \\ \langle I^{(2^4, 4)} \rangle &= \frac{1}{10} I^{(2^4, 0)} + \frac{1}{5} I^{(2^4, 1)} + \frac{1}{7} I^{(2^4, 2)} + \frac{1}{20} I^{(2^4, 3)} + \frac{71}{140} I^{(2^4, 4)}. \end{aligned}$$

As previously, we can write this as

$$\langle I^{(2^4, i)} \rangle = \sum_{j=0}^4 M_{ij} I^{(2^4, j)},$$

where M is a (non-orthogonal) projector (i.e. $M^2 = M$) with eigenvalues $(1, 1, 1, 0, 0)$.

Note that this result has an important physical consequence. Indeed, Slater integrals were derived under the assumption that the interaction potential is of Coulomb type. However, the conclusion that there are only 3 symmetrized $O(3)$ invariants are derived here for more general potentials. Indeed, we just assumed that the potential is real, spherically symmetric and invariant under the exchange of \mathbf{x} and \mathbf{y} , so that the D_4 symmetry holds. Any potential of the form $V(|\mathbf{x}|, |\mathbf{y}|, |\mathbf{x} - \mathbf{y}|) = V(|\mathbf{y}|, |\mathbf{x}|, |\mathbf{x} - \mathbf{y}|)$ satisfies these assumptions. As a consequence, we showed that the electronic interaction described by a large family of relaxed effective potentials can be described by the usual three Slater integrals F^0 , F^2 and F^4 for d orbitals.

C. Subduction from $O(3)$ to G

In this section, we consider the following problem. Let α be an irrep of G written in terms of spherical harmonics of an irrep of $O(3)$. For instance, if G is the cubic group O_h , then $\alpha = E_g$ and $\beta = T_{2g}$ can be written in terms of Y_ℓ^m with $\ell = 2$ (with the same radial parts). Let α come from ℓ_1 , β from ℓ_2 , γ from ℓ_3 and δ from ℓ_4 , we would like to know how to write the G -invariants $I^{(\alpha\beta\gamma\delta, \eta)}$ in terms of Slater integrals. In the following, we make the dependence on spherical harmonics explicit by using the notation $I^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta, \eta)}$.

1. Basis invariance

We first show that, for any group G (including $O(3)$), the G -invariants are basis independent. For that purpose, we define the projections onto an irrep α by

$$P^{(\alpha)} = \sum_a |\alpha a\rangle \langle \alpha a|.$$

According to³ (p. 84), there are basis states $|\alpha a\rangle$, $|\beta b\rangle$ and $|\eta e\rangle$ such that

$$(\alpha a \beta b | \eta e) = (\langle \alpha a | \otimes \langle \beta b |) | \eta e \rangle, \quad (\alpha a \beta b | \eta e)^* = \langle \eta e | (| \alpha a \rangle \otimes | \beta b \rangle).$$

We then obtain

$$I^{(\alpha\beta\gamma\delta, \eta)} = \frac{1}{\dim \eta} \text{Tr} \left(P^{(\eta)} (P^{(\alpha)} \otimes P^{(\beta)}) V (P^{(\gamma)} \otimes P^{(\delta)}) \right),$$

which is basis independent.

2. Isoscalar factors

As a consequence of basis independence, we can replace the basis $|\ell m\rangle$ of $O(3)$ by the basis $|\ell \alpha a\rangle$, where α runs over all the irreps of G that can be built from irrep ℓ of $O(3)$ and $a = 1, \dots, \dim \alpha$. Obviously, $O(3)$ is here just an example, and the same construction (called subduction) can be carried out for any group G' of which G is a subgroup. Subduction is useful to describe symmetry breaking.

We use the diagonalization formula in terms of subduction:

$$U_{abcd}^{(\ell_1\alpha\ell_2\beta\ell_3\gamma\ell_4\delta)} = \sum_{\ell\eta e} (\ell_1\alpha a \ell_2\beta b | \ell\eta e)^* (\ell_3\gamma c \ell_4\delta d | \ell\eta e) I^{(\ell_1\ell_2\ell_3\ell_4, \ell)}.$$

Now the Racah factorization lemma¹⁴ (p. 27) states that there are complex numbers $\begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix}$, called *isoscalar factors*, such that

$$(\ell_1 \alpha a \ell_2 \beta b | \ell \eta e) = \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix} (\alpha a \beta b | \eta e),$$

where $(\alpha a \beta b | \eta e)$ are Clebsch-Gordan coefficients of G . Isoscalar factors are fundamental ingredients of group-subgroup symmetry calculations^{12,14,20,27-29}. They satisfy important relations¹⁴ (p. 28)

$$\sum_{\ell} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha' & \beta' & | & \eta \end{pmatrix}^* = \delta_{\alpha\alpha'} \delta_{\beta\beta'},$$

$$\sum_{\alpha\beta} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell' \\ \alpha & \beta & | & \eta \end{pmatrix}^* = \delta_{\ell\ell'}.$$

Note that, in the first line, we assume that η belongs to the tensor product of α and β and, in the second line, that η can be obtained from ℓ by subduction. Isoscalar factors are usually calculated from Clebsch-Gordan coefficients, but their squares can be calculated from characters^{28,30}.

We can now write the Coulomb integrals in terms of isoscalar factors:

$$U_{abcd}^{(\ell_1 \alpha \ell_2 \beta \ell_3 \gamma \ell_4 \delta)} = \sum_{\ell \eta e} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix} \begin{pmatrix} \ell_3 & \ell_4 & | & \ell \\ \gamma & \delta & | & \eta \end{pmatrix}^* (\alpha a \beta b | \eta e) (\gamma c \delta d | \eta e)^* I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)}.$$

Therefore, the G -invariants can be expressed explicitly in terms of the $O(3)$ -invariants by a single sum

$$\begin{aligned} I^{(\ell_1 \alpha \ell_2 \beta \ell_3 \gamma \ell_4 \delta, \eta)} &= \frac{1}{\dim \eta} \sum_{abcde} U_{abcd}^{(\ell_1 \alpha \ell_2 \beta \ell_3 \gamma \ell_4 \delta)} (\alpha a \beta b | \eta e)^* (\gamma c \delta d | \eta e) \\ &= \sum_{\ell} \begin{pmatrix} \ell_1 & \ell_2 & | & \ell \\ \alpha & \beta & | & \eta \end{pmatrix} \begin{pmatrix} \ell_3 & \ell_4 & | & \ell \\ \gamma & \delta & | & \eta \end{pmatrix}^* I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)}, \end{aligned} \quad (38)$$

where the sum runs over all ℓ such that $|\ell_1 - \ell_2| \leq \ell \leq \ell_1 + \ell_2$ and irrep η of G can be built from spherical harmonics Y_{ℓ}^m . More precisely, since ℓ is a representation of $O(3)$ and G is a subgroup of $O(3)$, we can define a representation of G by the matrix $(-1)^g D_{m'm}^{\ell}(R_g)$ where R_g is the rotation corresponding to $g \in G$ and $(-1)^g$ is the sign corresponding to the transformation under inversion, if some element of G are not pure rotations. This representation is called the *subduced representation* of G from ℓ . This subduced representation is generally not an irreducible representation of G but it can be written as a sum of irreps of G , and η has to be one of these irreps.

To summarize the result of this section, $I^{(\ell_1 \alpha \ell_2 \beta \ell_3 \gamma \ell_4 \delta, \eta)}$ is the G -invariant obtained by assuming that the system has a symmetry group $O(3)$ larger than G . It can be used to determine how far the local symmetry G is from a spherical symmetry $O(3)$. Indeed, the number of independent parameters corresponding to spherical symmetry, $n^S(O(3))$, is smaller than the number of independent parameters $n^S(G)$ corresponding to G . The $O(3)$ -invariants $I^{(\ell_1 \ell_2 \ell_3 \ell_4, \ell)}$ (and their symmetrized version) can be used as parameters to fit the G -invariants $I^{(\alpha \beta \gamma \delta, \eta)}$ (and their symmetrized version). A fit with a small mean square error would mean that the Coulomb integrals are not far from spherically symmetric. A large error would mean that the G -irrep orbitals are strongly distorted from the spherical ones.

VI. CONCLUSION

Starting from the simple and familiar problem of calculating Coulomb integrals in the most economic way, we were led to use surprisingly sophisticated tools of group theory, such as Clebsch-Gordan coefficients, $6j$ -symbols, corepresentation theory and the Racah factorization theorem, and we had to recall the remarkable work by Derome and Sharp, which was unjustly forgotten. However, it was worth the effort because these tools enabled us to provide a completely general and explicit answer to the problem. We gave general formula instead of tables because tables would depend on the exact basis used for each irrep and on the phase choice of Clebsch-Gordan coefficients.

It would be tempting to extend the present treatment of real representation matrices to complex ones, for example by using their real and imaginary parts. We could even deal with pseudo-real irreps by using the fact that a representation and its complex conjugate of the representation are related by a similarity transformation. However, this would be a non-trivial extension of the present work, because the resulting real representations would not be irreducible and many of our proofs made a crucial use of Schur's lemma, which holds only for irreducible representations.

Another fruitful extension would be to deal with magnetic groups and their corepresentations, which are used to describe the transport and response properties of magnetic and multiferroic materials³¹⁻³⁵. Although we dealt with corepresentations in the present work, the theory of corepresentations is not as developed as the theory of representations, and this extension would also be non-trivial.

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- ³⁶ W. T. Sharp, *Racah algebra and the contraction of groups* (University of Toronto, Toronto, 1984).
- ³⁷ The relation between our Clebsch-Gordan coefficients and the $3j$ -symbols of Ref.¹⁰ is $(\alpha\beta\gamma|\eta e) = \sqrt{\dim\eta} \sum_{e'} (\alpha\beta\eta^*)_{abe'}^* (\eta)_{ee'}$, where $(\eta)_{ee'}$ is the so-called $1j$ -symbol.
- ³⁸ To be explicit, Derome's $1j$ -symbols $(\alpha)_{aa'}$ are different from Butler's $2jm$ -symbols $(\alpha_{aa'}^{\alpha\alpha'})$ because $1j$ -symbols are either symmetric or antisymmetric whereas $2jm$ -symbols can be chosen to be diagonal. Moreover, for real and complex representations, $1j$ -symbols are multiple of the identity, whereas this is not the case of $2jm$ -symbols. As a consequence, Derome and Sharp's $6j$ -symbols are better suited to our approach.
- ³⁹ Note that the formulas given in¹⁰ generalize the work by Sharp for quasi-ambivalent and multiplicity-free groups³⁶. All crystallographic point groups are quasi-ambivalent¹⁴ (p. 55).